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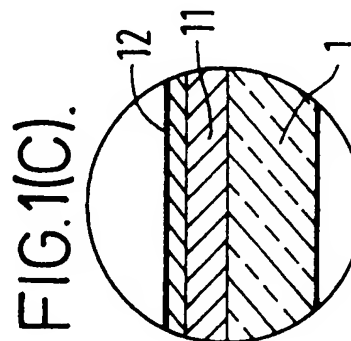
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HASELTINE LAKE & CO.
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London WC2A 1AT (GB)(54) **Fluorescent lamp.**

(57) There is disclosed a fluorescent lamp comprising:- a bulb (1) of glass containing more than 15% of sodium (Na); a mercury (Hg) vapour sealed in the bulb (1); a fluorescent layer (12) formed inside an inner surface of the bulb (1), the fluorescent layer (12) comprising a fluorescent material including a rare earth fluorescent material; and a protection layer (11) formed between the inner surface of the bulb (1) and the fluorescent layer (12), the protection layer (11) having a thickness of from 0.2 μ m to 1.5 μ m and comprising fine grains of a metal oxide which absorbs ultraviolet rays and thus prevents or slows down any decrease in lighting efficiency of the lamp.



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This invention relates to a fluorescent lamp with a fluorescent layer of a rare earth metal fluorescent substance, and a protection layer, both of which layers are coated on an inner surface of a bulb of the fluorescent lamp.

A fluorescent lamp with a protection layer is disclosed in JP-A-55-161352, in which the protection layer is composed of crystalline titanium oxide, which is coated on an inner surface of a glass bulb. A fluorescent layer is then formed on an inner surface of the protection layer and is made of a conventional halophosphor activated by Mn^{2+} and Sb^{2+} . The purpose of the protection layer is to prevent impurities contained in the glass bulb from diffusing into the fluorescent layer, as the impurities decrease the operating efficiency of the fluorescent layer.

A fluorescent lamp using soda-lime glass for the glass bulb, is well-known and disclosed, for example, in JP-A-58-19850. Soda-lime glass contains little or no lead oxide (PbO) (which is an expensive material) and therefore the use of soda-lime glass reduces the manufacturing costs and also prevents environmental pollution caused by the scrapping of bulbs. However, soda-lime glass contains about 15-17% by weight of sodium (Na), which is three times the amount of sodium contained in lead glass, which is also used for making fluorescent lamps. The sodium (Na) contained in soda-lime glass diffuses into the fluorescent layer formed on the inner surface of the bulb when the bulb is heated during its manufacture and its operation. This diffused sodium reacts with elements of the fluorescent layer and reduces the luminous efficiency of the fluorescent layer. This sodium (Na) becomes an amalgam owing to the reaction with mercury (Hg) in the discharge space of the lamp, and the resulting amalgam constitutes coloured portions of the inner surface of the bulb. The coloured portions consequently increase the loss of transmission of light. The diffusion of sodium (Na) as described above is increased by ultraviolet irradiation from the bulb, in addition to heating. Furthermore, the thickness of the fluorescent layer using a rare earth metal fluorescent substance is thin in comparison with other fluorescent layers using a halophosphate phosphor activated by Mn^{2+} and Sb^{2+} . As a result, mercury (Hg) diffuses through the fluorescent layer and reacts with sodium which has diffused to the inner surface of the bulb. The amalgam resulting from this reaction also creates coloured portions on the bulb which reduce light transmission. Consequently, in bulbs in which the fluorescent layer is composed of a rare earth metal, the light emission of the fluorescent lamp decreases in proportion to its amount of use.

A fluorescent lamp having a protection layer absorbing ultraviolet rays for preventing the diffusion of sodium (Na) is described in JP-A-50-12885. However, this fluorescent lamp uses a halophosphate

phosphor activated by Mn^{2+} and Sb^{2+} which is conventional and the protection layer is made by special methods including a baking step and is, therefore, extremely thin. Thus, this technique cannot be easily applied to the fluorescent lamp using a rare earth metal fluorescent substance and the protection layer cannot be made by such special methods.

US-A-5051650 and US-A-5227693 disclose other types of fluorescent lamp using a protection layer for preventing ultraviolet rays from emitting from the lamp. The protection layer comprises a mixture of particles of titanium oxide (TiO_2) and zinc oxide (ZnO). The fluorescent substance of the lamp comprises a rare earth metal fluorescent substance. However, the lamp is supposed to use a lead glass, for easily bending or connecting the glass. Further, the protection layer is very thick as the protection layer is intended to prevent more than 90% of ultraviolet rays from emitting from the lamp. The efficiency of this lamp is lower than that of a fluorescent lamp without the protection layer because of the thick protection layer absorbing visible light.

According to the present invention, there is provided a fluorescent lamp comprising:

a bulb formed of glass containing at least 15% by weight of sodium;

mercury vapour and a rare gas sealed in the bulb;

a fluorescent layer formed inside an inner surface of the bulb, the fluorescent layer comprising a fluorescent material including a rare earth metal fluorescent material; and

a protection layer formed between the inner surface of the bulb and the fluorescent layer;

characterized by the protection layer having a thickness of from $0.2\mu m$ to $1.5\mu m$ and comprising fine grains of a metal oxide which absorbs ultraviolet rays.

The present invention can thus provide a fluorescent lamp in which reduction of luminous efficiency, due to interaction between mercury (Hg) and sodium (Na), is prevented or reduced.

A preferred example of the metal oxide is at least one oxide selected from zinc oxide and titanium oxide. The metal oxide of the protection layer is preferably a mixture of zinc oxide and titanium oxide in which the zinc oxide is more than 50% by weight.

The fluorescent layer can include cerium.

In the lamp of the present invention, the fluorescent material contains a rare earth metal fluorescent material preferably capable of emitting three kinds of visible light corresponding to blue, green and red. Preferably more than 90% by weight of fluorescent layer is constituted by the rare earth metal fluorescent material.

Preferably more than 90% by weight of the protection layer is constituted by the fine grains of metal oxide.

For a better understanding of the present inven-

tion and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawings, in which:-

Figs. 1(a) and 1(b) are longitudinal sectional and cross sectional views, respectively, of an embodiment of the fluorescent lamp according to the present invention;

Fig. 1(c) shows an enlargement of that part of the lamp in the circle C in Figure 1; and

Fig. 2 is a graph showing the amount of light output of the fluorescent lamp of the embodiment shown in Figures 1(a) and 1(b) and of other lamps, as a function of lamp lifetime.

Figs. 1(a) and 1(b) show an embodiment of the present invention in which a fluorescent layer is formed inside an inner surface of a bulb 1 composed of soda lime glass comprising about 15-17% by weight of sodium (Na). Bulb 1 is formed as a straight tube. A flarestem 2 is inserted to form an air-tight seal at both ends of the bulb 1. A pair of lead wires 3 penetrates through the flarestem 2 at both ends of the bulb 1 without disruption of the air-tight seal. A respective filament electrode 4 is connected to and supported by the pair of lead wires 3 at each end of the bulb 1. Each filament electrode 4 is made of tungsten (W) or any conventional composition used for filament electrodes. An electron emitter substrate such as BaO, SrO or CaO, is added to the filament electrode 4. Two metal caps 5 are attached at the opposite ends of the bulb 1. A pair of pins 6 passes through each metal cap 5 and is insulated therefrom, and the pins 6 are electrically connected to each pair of lead wires 3.

A protection layer 11 is formed on the inner surface of the bulb 1, and comprises fine metal oxide grains which absorb ultraviolet rays. A fluorescent layer 12 is formed on the protection layer 11, and comprises a rare earth metal fluorescent substance.

In the illustrated embodiment, the protection layer 11 comprises fine metal oxide grains of zinc oxide (ZnO), titanium oxide (TiO₂) or a mixture of these metal oxide. The average particle size of fine metal oxide grains is less than 0.1 μm. The zinc oxide (ZnO) grains are highly absorptive of ultraviolet rays, but have very low absorption of visible light. The zinc oxide (ZnO) is the preferred material for the structure of the protection layer 11 in this embodiment. Metal oxide materials for the protection layer 11 other than zinc oxide (ZnO) or titanium oxide (TiO₂) cause a larger absorption of visible radiation. In the illustrated embodiment, the protection layer 11 has a thickness of less than 0.5 μm. In order to form the protection layer 11, the fine metal oxide grains are dispersed in a disperse medium such as water to form a mixture. Next, the mixture is coated on the inner surface of the bulb 1 and the coated layer is dried thereafter. Finally, only fine grains remain in the protection layer 11 and are accumulated to form the protection layer 11. The fine

grains of protection layer 11 adhere to the inner surface of the bulb 1 by the effect of van der Waals' force.

The fluorescent layer 12 includes three kinds of rare earth metal phosphors for emitting red light, green light and blue light during lamp operation. The phosphor for emitting red light is yttrium oxide (Y₂O₃) or yttrium oxide activated by europium (Y₂O₃:Eu). The phosphor for emitting blue light is an alkaline earth halophosphate phosphor activated by divalent europium (which phosphor is disclosed in US-A-4038204) or an alkaline earth aluminate phosphor activated by divalent europium (BaMg₂Al₁₆O₂₇:Eu) (which phosphor is disclosed in US-A-4216408). The phosphor for emitting green light is represented by the chemical formula (La, Ce, Tb) . (P,Si)O₄. The fine grains of these three kinds of phosphors are mixed.

In the structure of this fluorescent lamp, the protection layer 11 having an absorptive property of ultraviolet rays is formed between the inner surface of the bulb 1 and the fluorescent layer 12; therefore, protection layer 11 prevents direct contact between the inner surface of the bulb 1 and the fluorescent layer 12, and absorbs ultraviolet rays which would otherwise reach the inner surface of bulb 1 through the fluorescent layer 12. Consequently, the diffusion of sodium (Na) from the bulb 1 made of soda-lime glass, which would be caused by ultraviolet rays, is reduced. Protection layer 11 blocks direct contact between mercury (Hg) and diffused sodium (Na) and, therefore, the occurrence of coloured or blackened portions on the inner surface of the bulb 1 is reduced or prevented, and a maintenance ratio of light output is maintained high.

Protection layer 11 comprises substantially no binder and thus is different from the disclosure in US-A-5051650, so that there are substantially no diffused impurities of the binder on an inner surface of the bulb 1. As the protection layer 11 does not include a binder, it is possible to employ no heating or only low temperature heating during formation of protection layer 11 and, therefore, diffusion of sodium (Na) from bulb 1, which would otherwise result from such high temperature heating like a baking step, is avoided.

Thus the protection layer 11 is substantially composed of only fine grains, and impurities are scarcely present in the protection layer 11. Therefore, the likelihood of blackening or short life of the lamp is low as compared with a fluorescent lamp with a protection layer including a binder such as that of US-A-5051650 and a fluorescent lamp with a protection layer formed by a special method including a baking step for baking an organometallic compound. The term "substantially" means that protection layer 11 contains more than 90% by weight of the fine grains of the metal oxide.

The fluorescent layer 12 comprising the rare earth metal phosphors can be formed thinner than previously used conventional fluorescent layers such as a halophosphate phosphor activated by manga-

nese and antimonide. The fluorescent layer 12 can be formed thinner (for example 10-25 μ m) because the particle size (3-5 μ m) of the fine grains of the rare earth metal phosphors is smaller than the grains (particle size: 7-10 μ m) of conventional fluorescent layers (having a thickness of 30-70 μ m). However, the probability of mercury (Hg) passing through the fluorescent 12 comprising rare earth metal phosphors becomes larger as fluorescent layer 12 is formed thinner, but nevertheless the reaction between mercury (Hg) in bulb 1 and sodium (Na) diffused from the bulb is reduced in view of the presence of the protection layer 11.

Protection layer 11 comprising fine grains of zinc oxide (ZnO) or titanium oxide (TiO₂), or a mixture of both, has a high absorptive property of ultraviolet rays and substantially no absorption of visible light, and enables provision of a fluorescent lamp having a high lighting efficiency.

Protection layer 11 comprising a mixture of fine grains of zinc oxide (ZnO) and titanium oxide (TiO₂) has a fine structure and high strength, due to the fine grains of the zinc and titanium oxides. Furthermore, protection layer 11 does not cause an undesirable interference fringe because the fine grains of the zinc oxide (ZnO) and titanium oxide (TiO₂) have respectively different average particle sizes. In this embodiment, the average particle size of fine grains of the zinc oxide is about 0.04 μ m and that of titanium oxide is about 0.1 μ m. The particle size is measured by photography with an electron microscope. In this case, the protection layer 11 provides high transmission of effective visible radiation owing to absorption of ultraviolet rays and substantially no absorption of visible light, especially when the quantity of zinc oxide (ZnO) is more than 50% by weight of the mixture of the zinc and titanium oxides.

A protection layer 11 having a thickness of more than 1.5 μ m causes an undesirable excessive absorption of visible light. On the contrary, a protection layer 11 having a thickness of less than 0.2 μ m permits too much ultraviolet rays to pass therethrough. A more desirable thickness for the protection layer 11 is between 0.5 and 1.0 μ m. By way of comparison, a conventional protection layer used in conjunction with a conventional fluorescent material to intercept ultraviolet rays including near visible light, required a thickness of more than 1.5 μ m. Consequently, the conventional protection layer was made thick with the consequential disadvantage of visible light absorption. In contrast, in accordance with the present invention, protection layer 11 is capable of absorbing short wavelength ultraviolet rays which makes sodium (Na) diffuse more than others. Therefore, even a thin protection layer 11 has effects which are possible to prevent diffusion of sodium (Na) and to reduce reaction with mercury (Hg).

Fig. 2 shows graphically the relationship between

the life of four fluorescent lamps and the light output thereof; the vertical axis shows the light output (Lm), and horizontal axis shows the lifetime in hours (hr). The lamp structure of type-a is an embodiment of this invention having a protection layer of less than 0.5 μ m thickness, of type-b has no protection layer, of type-c has a protection layer using easily absorbed Al₂O₃ as fine metal oxide grains, and of type-d has a protection layer which comprises fine metal oxide grains of zinc oxide (ZnO) and titanium oxide (TiO₂) such as taught by this invention, but having a thickness of 1.0 μ m. The remaining structure and electrical properties of each lamp is the same for types a-d.

Fig. 2 suggests that protection layer 11 having a thickness more than necessary does not have an effect of increasing the maintenance of the light output. By comparison of type-a with type-d, an increased thickness protection layer 11 results in reduced visible light output both initially and during the lamp life. By comparison of type-a with type-c, type-a is recognized as providing an increased maintenance of the light output as compared with type-c.

Fluorescent layer 12 comprising cerium (Ce) as a phosphor for green light is effective for practising this invention. Although cerium phosphor also radiates 300-380nm as ultraviolet rays, protection layer 11 absorbs this ultraviolet radiation.

Claims

1. A fluorescent lamp comprising:
 - a bulb (1) formed of glass containing at least 15% by weight of sodium;
 - mercury vapour and a rare gas sealed in the bulb (1);
 - a fluorescent layer (12) formed inside an inner surface of the bulb (1), the fluorescent layer (12) comprising a fluorescent material including a rare earth metal fluorescent material; and
 - a protection layer (11) formed between the inner surface of the bulb (1) and the fluorescent layer (12);
 characterized by the protection layer (11) having a thickness of from 0.2 μ m to 1.5 μ m and comprising fine grains of a metal oxide which absorbs ultraviolet rays.
2. A fluorescent lamp according to claim 1, characterized in that the fine grains of metal oxide comprise at least one metal oxide selected from zinc oxide and titanium oxide.
3. A fluorescent lamp according to claim 1 or 2, characterized in that the fine grains of metal oxide comprise a mixture of zinc oxide and titanium oxide, in which zinc oxide is more than 50% by weight.

4. A fluorescent lamp according to claim 1, 2 or 3, characterized in that the fine grains comprise a mixture of fine grains of two kinds of metal oxide, with an average particle size of fine grains of one or the metal oxides being different from that of the other. 5
5. A fluorescent lamp according to any one of claims 1 to 4, characterized in that the average particle size of the fine grains is less than $0.1\mu\text{m}$. 10
6. A fluorescent lamp according to any one of claims 1 to 5, characterized in that the protection layer (11) is free from a binder. 15
7. A fluorescent lamp according to any preceding claim, characterized in that more than 90% by weight of the protection layer is constituted by the fine grains of metal oxide. 20
8. A fluorescent lamp according to any preceding claim, characterized in that the fluorescent material includes a mixture of rare earth phosphors for emitting blue, green and red light. 25
9. A fluorescent lamp according to claim 8, characterized in that said mixture of rare earth phosphors includes a cerium phosphor for emitting green light. 30
10. A fluorescent lamp according to any preceding claim, characterized in that more than 90% by weight of the fluorescent layer (12) is constituted by the rare earth metal fluorescent material. 35

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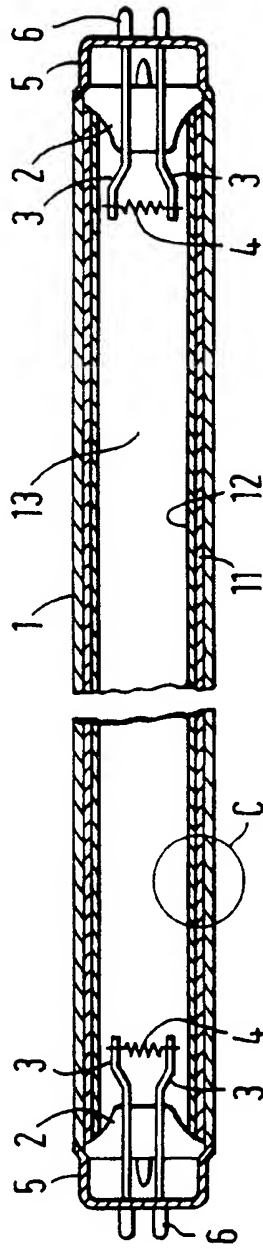


FIG. 1(A).

FIG. 1(C).

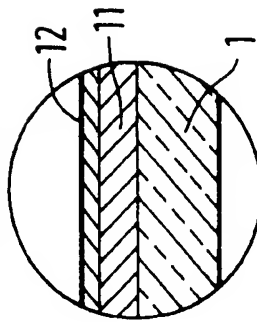


FIG. 1(B).

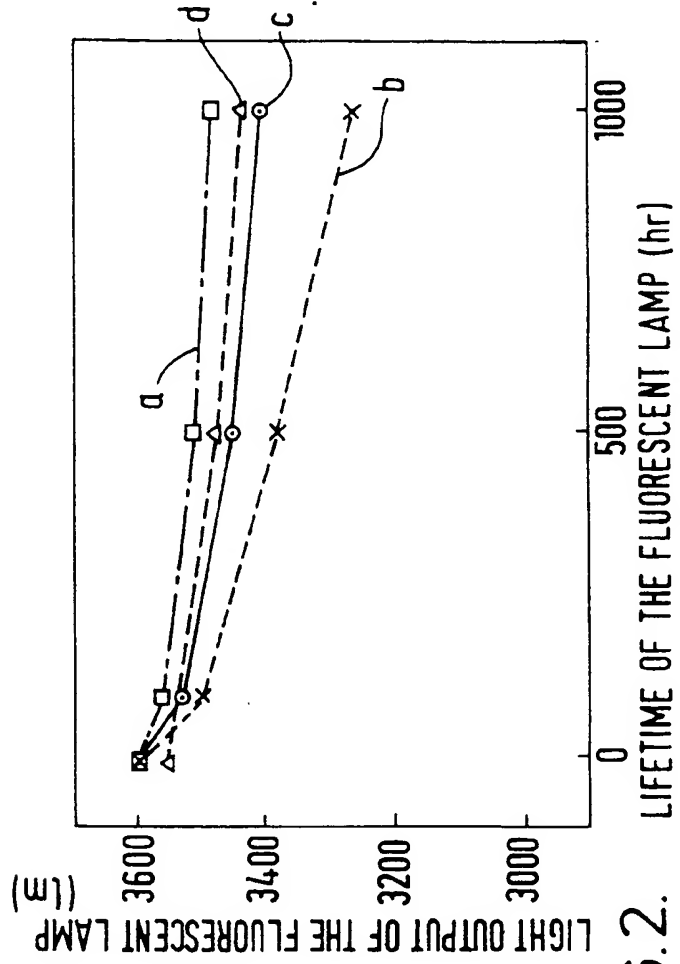
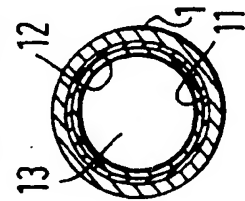


FIG. 2.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 30 2234

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	EP-A-0 449 307 (TOSHIBA LIGHTING) * abstract * * page 2, line 55 - page 3, line 15 * * page 4, line 34 - page 5, line 2 * * page 6, line 5 - line 11; figure 1 * ---	1,2,4,5, 8,9	H01J61/40 H01J61/35
A	US-A-3 141 990 (RAY) * column 1, paragraph 1 - column 2, paragraph 1 * * column 2, line 63 - column 3, line 21; figures 1,2 * ---	1,2,5	
A	US-A-3 748 518 (LEWIS) * abstract; figure 1 * * column 1, paragraph 2 - column 2, paragraph 4 * * column 2, line 63 - column 3, line 52 * ---	1	
A	US-A-4 289 991 (SCHREURS) * abstract * * column 3, paragraph 1 - paragraph 2 * -----	6	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			H01J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27 June 1994	Examiner Greiser, N
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons & : member of the same patent family, corresponding document	

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